Debromination of PBDEs in anaerobic sediment microcosms

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Introduction.

Over the last few years concern has arisen over the environmental fate and effects of brominated flame retardants. Polybrominated diphenyl ether (PBDE) flame retardants in the aquatic environment accumulate in sediments and biota. Degradation reactions in anaerobic sediments could potentially play an important role in the environmental fate of these compounds. Reductive debromination of PBDEs has been reported in the gut of carp, presumably by anaerobic bacteria (Stapleton et al. 2004) and in anaerobic activated sludge (Gericke et al. 2005). We have previously presented evidence for the reductive debromination of PBDEs in anaerobic suspensions of sediment from the Western Scheldt estuary (Skoczynska et al. 2005). In this study we investigated the formation of debrominated products from deca- and nonabromodiphenyl ethers in these sediment microcosms.

Materials and Methods.

Sediment incubations consisted of 10 g Western Scheldt sediment (sampled near Hansweert) suspended in 50 ml anaerobic medium with a mixture of acetate, lactate and pyruvate as electron donors. The suspensions were spiked with 14.0 μg/g decabromodiphenyl ether (BDE 209) and incubated anaerobically at room temperature in the dark. Autoclaved suspensions were incubated as sterile controls. Similar incubations were started with the nonabrominated diphenyl ethers BDE 206 (2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether, 11.6 μg/g), BDE 207 (2,2',3,3',4,4',5',6,6'-nonabromodiphenyl ether, 11.0 μg/g) and BDE 208 (2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether, 10.4 μg/g). In addition, a strongly sorbing compound (benzo[e]pyrene) was added to some incubation with BDE-209 in order to investigate whether this would enhance the bioavailability and thus the degradation of the PBDEs already present in the sediment. The anaerobic sediment suspensions (viable and sterile) were spiked with 29.16 μg benzo[e]pyrene (in 300 μl acetone with c= 97.2 μg/ml). At appropriate times incubations were terminated and duplicate sediment samples of viable cultures and sterilised controls were analysed for PBDEs and PAHs.

The incubations were terminated by acidification with HCl. Sediment samples after medium removal were spiked with ^{13}C internal standard (150 and 100 μl in different incubations). The ^{13}C-internal standard was obtained from Wellington laboratories. The whole sediment samples were extracted using a shaker at ca. 220 rpm with 60 ml acetone for ca. 12 hours and with 60 ml pentane for 2 hours. Subsequently, the medium was added again to obtain better phase separation and the samples were centrifuged at 2000 rpm.

PBDEs were analysed with a GC coupled with a single quadrupole mass spectrometer (Thermo Quest) in selected ion monitoring mode. The GC was operated in cold on-column injection mode and was equipped with 15m DB-1HT capillary column (inside diameter of 0.25 mm and phase thickness of 0.1 μm). The GC-MS interface temperature was set at 280°C and the source temperature at 250°C. For the measurements of deca- and nona-BDEs the following multistage temperature program was used: the initial temperature was 90°C and this temperature was maintained for 0.5 min. The tempera-

ture was then increased at a rate of 15°C/min to 295°C, then at a rate of 4°C/min to 320°C and then at a rate of 10°C/min to 325°C and was kept at 325°C for 2 min. The flow rate was 0.7 ml/min. For the measurements of the lower brominated BDE's we used the following multistage temperature program: the initial temperature was 80°C and the temperature was increased at a rate of 10°C/min to 180°C, then at a rate of 4°C/min to 270°C and then at a rate of 10°C/min to 320°C and was kept at 320°C for 20 min. The flow rate was 1.30 ml/min.

Results and Discussion.

Methane production was observed (data not shown) in the viable incubations as well as in the sterile incubations spiked with BDEs 209, 208, 207 and 206 and incubated for nine months. However the CH_4 concentrations in the latter were approximately 10 times lower than in viable concentrations indicating reduced microbial activity in the autoclaved suspensions. There was no measurable decrease in the concentrations of the added BDEs in both sterile and in viable incubations. However, nonabrominated congeners were measured in the BDE 209 incubations at concentrations that were much higher than the background level of these congeners (Fig. 1). These peaks were identified as the three nonabrominated congeners BDE 206, BDE 207 and BDE 208 by comparison of their retention times and mass spectra with those of authentic standards. No octabrominated congeners were detected in either the sampled sediment or in the incubations with BDE 209.

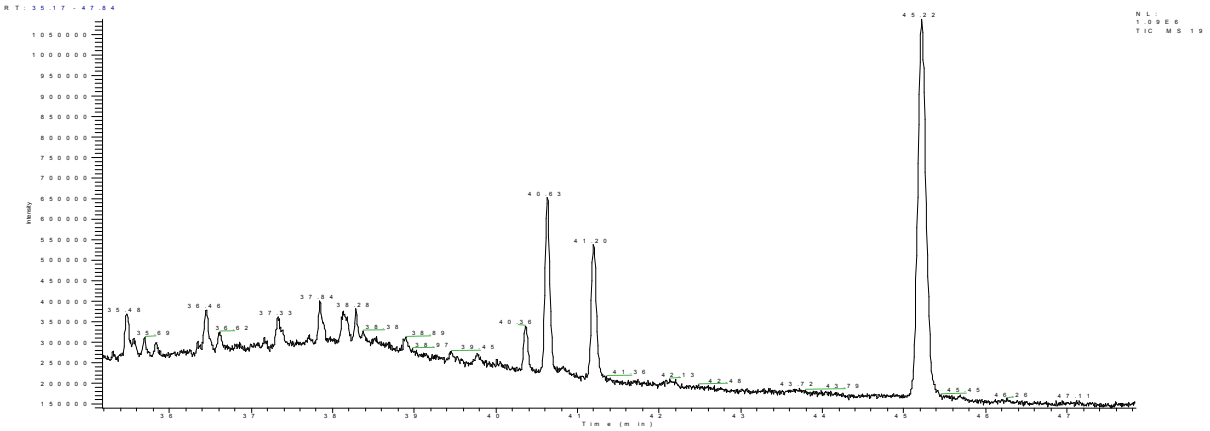

Fig. 1. Formation of debrominated products from decabromodiphenyl ether (BDE 209).

Octabrominated congeners were, however, detected in the incubations with nonabrominated BDEs. Different fingerprints of octabrominated congeners were present in sediments exposed to the different nonabrominated PBDEs. This suggests that the octabrominated congeners could be formed by debromination of the original nonabrominated congener. BDE 201, BDE 203 and/or BDE 198 (overlapping retention time) were identified in BDE 208 incubations. In BDE 207 incubations BDE 201, BDE 196, BDE 197 and/or BDE 204, BDE 203 and/or BDE 198 were found. Finally, BDE 196, BDE 205, BDE 203 and/or 198 were found in the incubations with BDE 206. Other peaks in chromatograms identified as octabrominated congeners, could not be assigned to the particular congeners because of the lack of standards.

Interestingly, a significant decrease in the concentration of native BDE 209 was observed in the incubations with nonabrominated BDEs (e.g. Fig. 2). This may indicate that the added congeners stimulate the degradation of BDE 209 already present in the sediment, either by stimulating microbial activity or by displacing BDE 209 from sorption sites.

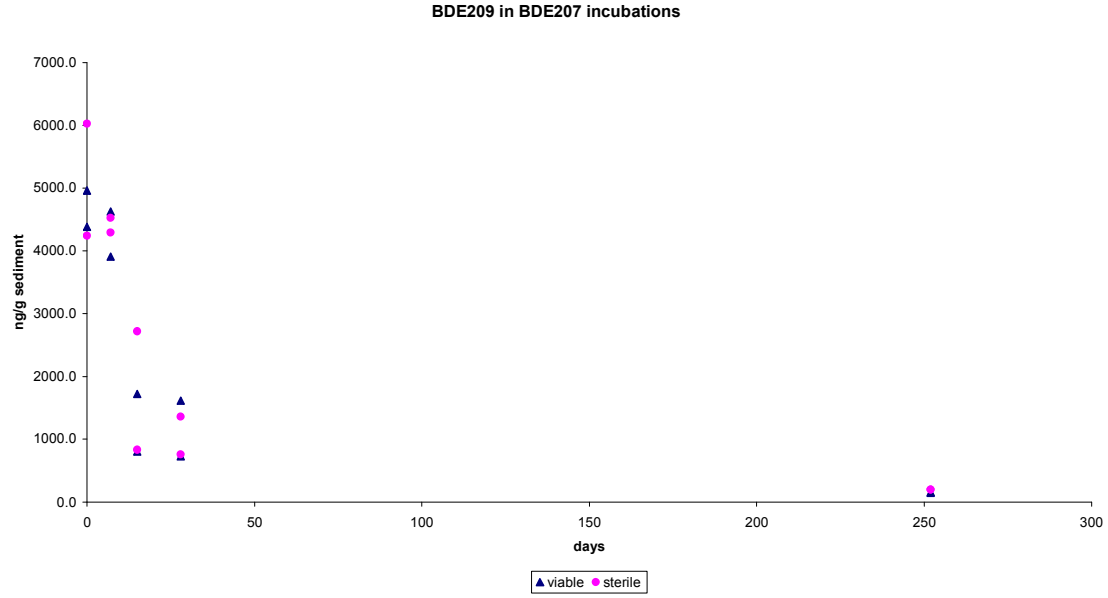

Fig. 2. Removal of BDE 209 in sediment suspensions incubated with BDE 207

In order to investigate whether the addition of a strongly sorbing compound would stimulate debromination of native sorbed PBDEs, a relatively high concentration of benzo[e]pyrene (approximately 3 µg/g sediment) was added to anaerobic sediment suspensions. The suspensions showed very high levels of methane production (20% methane in the headspace after 3 months) in the viable suspensions and none in the sterile cultures. However, after a total of 251 days there was no significant change in the levels of BDE 209 in both viable and sterile incubations. In contrast, the levels of the nonabrominated congeners did decline and were under the detection level after 136 days, but no octabrominated congeners were detected.

The results of these experiments are inconsistent and it is possible that the low removal of PBDEs sometimes observed is related to the restricted bioavailability of these highly sorbing compounds. In this regard it may be advantageous to study this process in sediment-free systems or alternatively to quantify the bioavailability of the compounds during the experiment. Nevertheless, these results seem to indicate that there is a potential for debromination of PBDEs in Western Scheldt sediments. Although this process could contribute significantly to the removal of PBDEs from the environment, it may also be a reason for concern, as it would convert the relatively poorly bioavailable BDE 209 into congeners more readily taken up by biota.

Acknowledgement.

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